Electronic Supplementary Information

Supramolecular Assemblies Controlled by Cucurbit[*n*]uril Size (n = 6, 7, 8 and 10)

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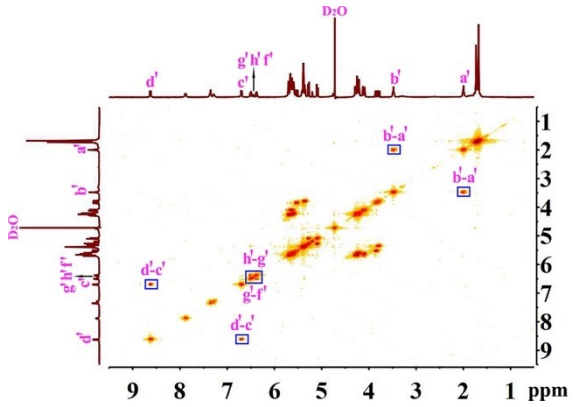

Figure S1. The COSY spectrum of **G** with 2.22 equivalents of TMeQ[6] in D_2O (400 MHz).

	H_a	H_b	H_c	H_d	H_e	H_f	H_{gh}
free **G**	1.97	3.40	6.64	7.92	5.21	7.27	7.37
G with 1.00 equiv. TMeQ[6]	2.01	3.49	6.71	8.65	4.74	6.39	6.52, 6.46
field shift	-0.04	-0.09	-0.07	-0.73	0.47	0.88	0.85, 0.91
G with 1.00 equiv. Q[7]	1.85	3.02	6.16	7.68	4.88	6.80	7.06
field shift	0.12	0.38	0.48	0.24	0.33	0.47	0.31

Table S1. ^1H NMR spectral changes observed for the **G**@TMeQ[6] system on addition of one equivalent of TMeQ[6] and the **G**@Q[7] system on addition of one equivalent of Q[7].

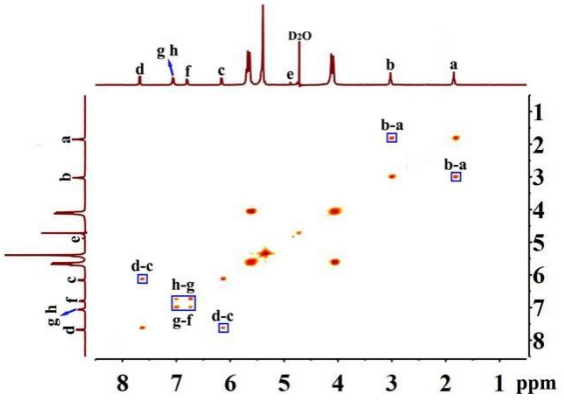

Figure S2. The COSY spectrums of **G** with 1.706 equivalent of Q[7] in D_2O (400 MHz).

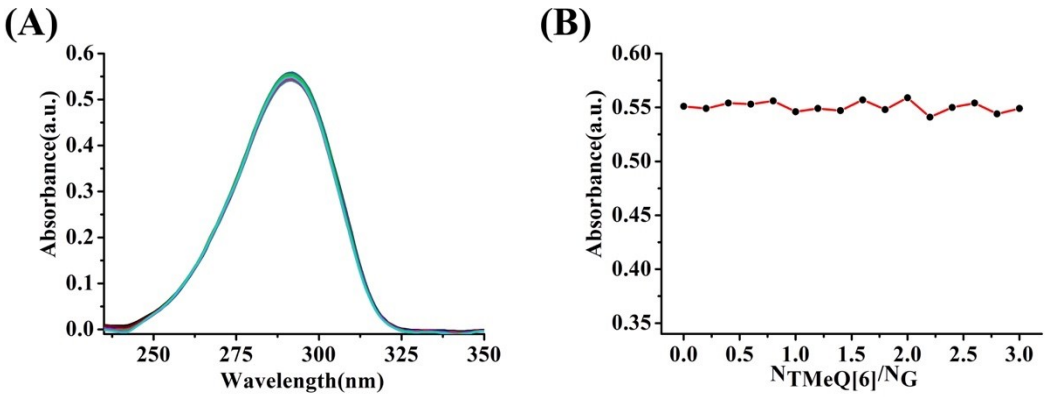

Figure S3. (Colour online) (A) Electronic absorption of **G** (2×10^{-5} mol L^{-1}) upon addition of increasing amounts (0, 0.2, 0.4⋯⋯2.6, 2.8, 3.0 equivalents) of TMeQ[6]; (B) concentration and absorbance *vs*. $N_{TMeQ[6]}/N_G$ plots.

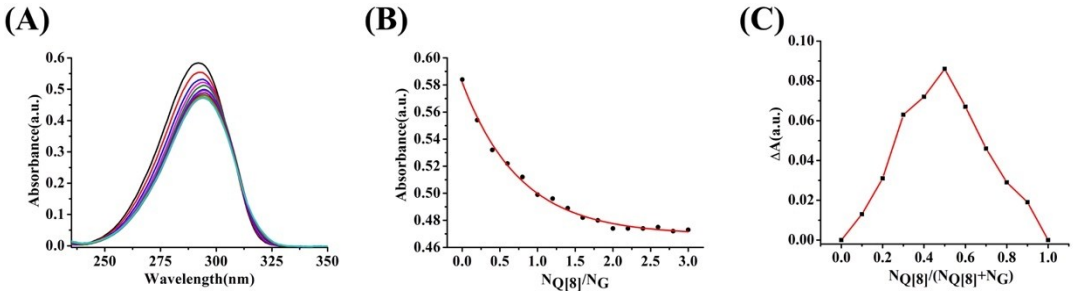

Figure S4. (Colour online) (A) Electronic absorption of **G** (2×10^{-5} mol L^{-1}) upon addition of increasing amounts (0, 0.2, 0.4⋯⋯2.6, 2.8, 3.0 equivalents) of Q[8]; (B) concentration and absorbance *vs*. $N_{Q[8]}/N_G$ plots; (C) the corresponding $\Delta A–N_{Q[8]}/(N_{Q[8]} + N_G)$ curves.

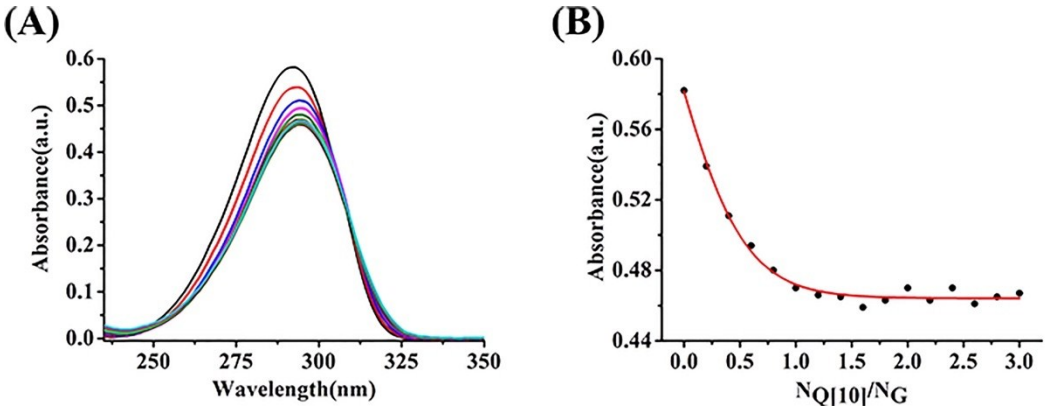

Figure S5. (Colour online) (A) Electronic absorption of **G** (2×10^{-5} mol L^{-1}) upon addition of increasing amounts (0, 0.2, 0.4⋯⋯2.6, 2.8, 3.0 equivalents) of Q[10]; (B) concentration and absorbance *vs*. $N_{Q[10]}/N_G$ plots.

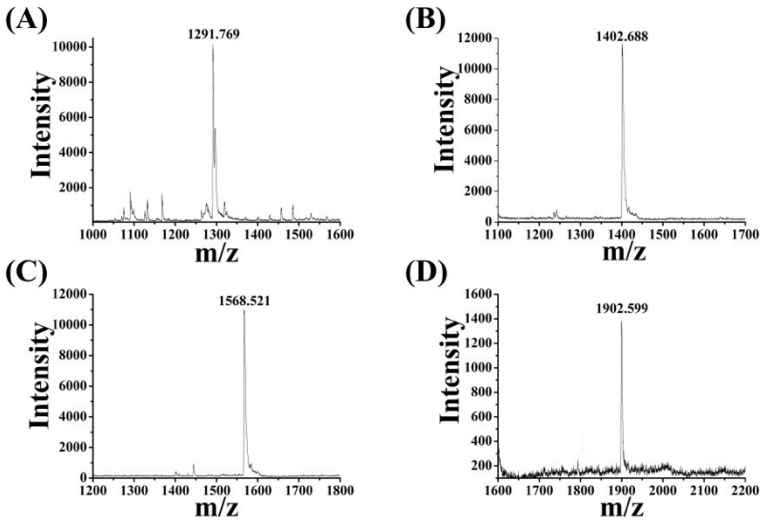

Figure S6. MALDI-TOF mass spectra of TMeQ[6]@**G** (A), Q[7]@**G** (B), Q[8]@**G** (C) and Q[10]@**G** (D).

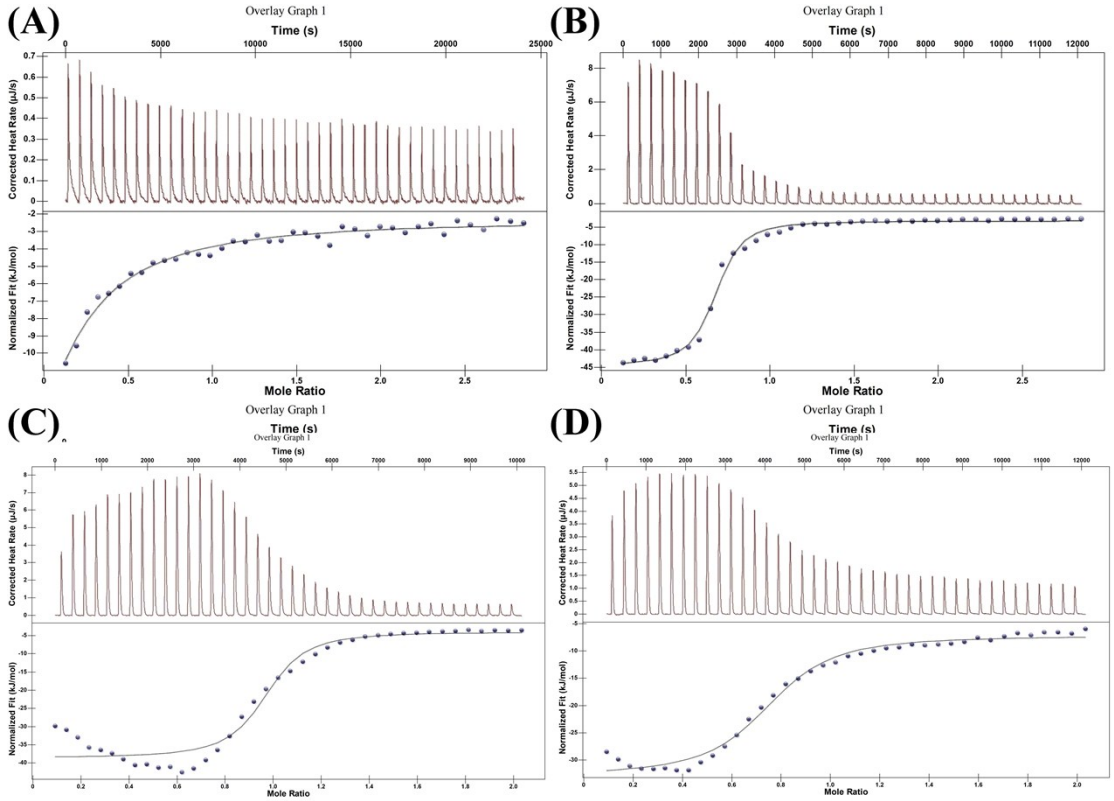

Figure S7. ITC data for the binding of **G** with Q[*n*] (TMeQ[6], Q[7], Q[8], Q[10]) in aqueous solution.

Host	guest	K_a (M^{-1})	Ref
Q[8]	g1	1.541×10^4	1
	g2	4.714×10^5	
	g3	8.477×10^5	
	g4	5.541×10^6	
	g5	5.597×10^6	
	g6	3.333×10^6	
TMeQ[6]	g2	$(4.23\pm0.6)\times10^5$	2
	g3	$(1.08\pm0.32)\times10^6$	
TMeQ[6]	G	$(1.98\pm0.5)\times10^4$	In this work
Q[7]		$(1.07\pm0.4)\times10^6$	
Q[8]		$(1.39\pm0.8)\times10^6$	
Q[10]		$(3.03\pm0.6)\times10^5$	

Table S2. Binding constant values of cucurbit[*n*]urils with some alkyl-substituted 4-pyrrolidinopyridinium salts by ITC. 4-(C_4H_8N)C_5H_5NRBr, R=Et (g1), *n*-butyl (g2), *n*-pentyl (g3), *n*-hexyl (g4), *n*-octyl (g5), *n*-dodecyl (g6).

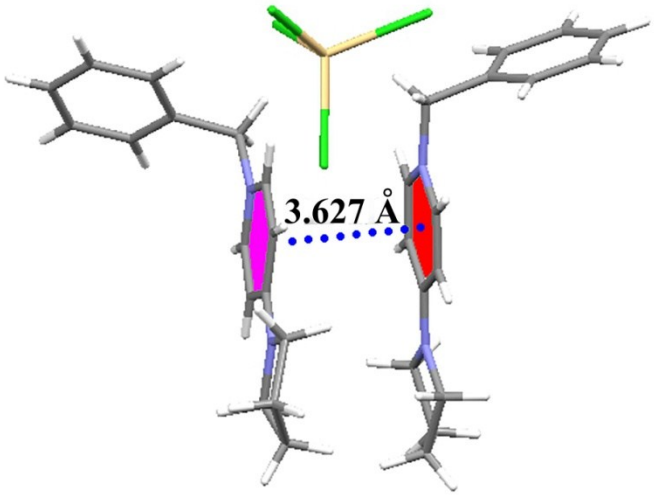

Figure S8. Single crystal X-ray structure of [$\mathbf{G}_2$][$CdCl_4$] showing a π...π interaction.

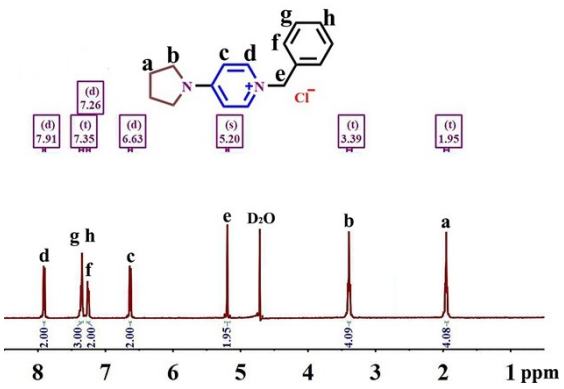

Figure S9. ^{1}H NMR spectrum of **G** in D_2O (400 MHz).

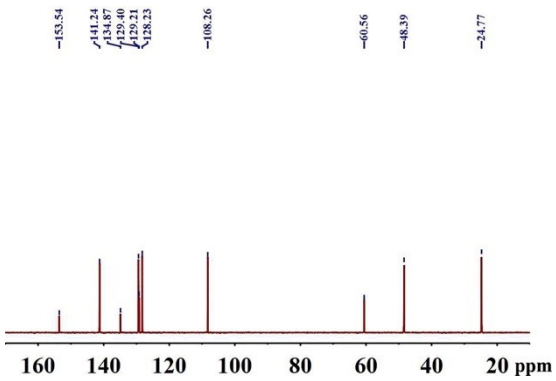

Figure S10. ^{13}C NMR spectrum of **G** in D_2O (400 MHz).

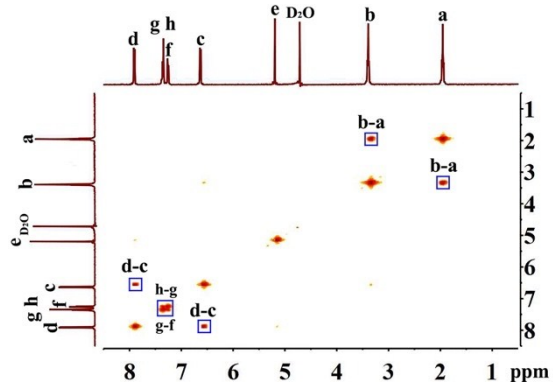

Figure S11. COSY spectrum of **G** in D_2O (400 MHz).

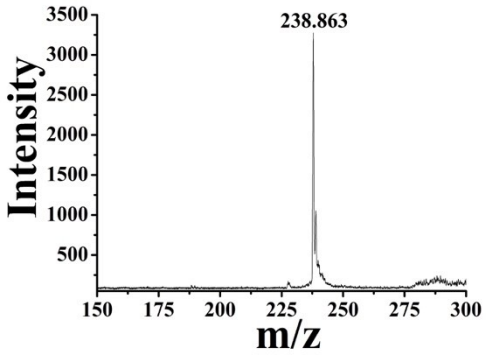

Figure S12. Mass spectrometry of **G** in H_2O.

References

[1] W. Xu, J. Kan, B. Yang, T. J. Prior, B. Bian, X. Xiao, Z. Tao and C. Redshaw, *Chem. Asian J.* **2019**, *14*, 235–242.

[2] B. Yang, X. Xiao, Y.-Q. Zhang, Q.-J. Zhu, S.-F. Xue, Z. Tao and G. Wei, *RSC Adv.*, **2014**, *4*, 44359-44366.